On the origin of unusual transport properties observed in densely packed polycrystalline $CaAl_2$

S. Sergeenkov
Centro Multidisciplinar para o Desenvolvimento de Materiais Ceramicos, Departamento de Física, Universidade Federal de São Carlos, 13565-905 São Carlos, SP, Brazil and Joint Institute for Nuclear Research, Bogoliubov Laboratory of Theoretical Physics, 141980 Dubna, Moscow region, Russia

F.M. Araujo-Moreira
Centro Multidisciplinar para o Desenvolvimento de Materiais Ceramicos, Departamento de Física, Universidade Federal de São Carlos, 13565-905 São Carlos, SP, Brazil

(Dated: February 6, 2008)

A possible origin of unusual temperature behavior of transport coefficients observed in densely packed polycrystalline $CaAl_2$ compound [M. Ausloos et al., J. Appl. Phys. **96**, 7338 (2004)] is discussed, including a power-like dependence of resistivity with $\rho \propto T^{-3/4}$ and N-like form of the thermopower. All these features are found to be in good agreement with the Shklovskii-Efros localization scenario assuming polaron-mediated hopping processes controlled by the Debye energy.

PACS numbers: 71.30.+h, 72.15.Eb, 72.20.-i

After the discovery of superconductivity in MgB_2, a search began for other intermetallic compounds with similar structure or lattice symmetry (see, e.g.[1,2,3,4,5,6] and further references therein). In particular, a class of pseudoternary compounds $CaAl_{2-x}Si_x$ with $C32$ structure is shown[3,5] to exhibit superconducting behavior for $x > 0.5$. The structural and thermodynamic investigations confirmed a BCS-type pairing mechanism in these compounds with a rather strong electron-phonon coupling[6]. At the same time, using an original route (which allowed formation of crystalline rather than glassy phase), tiny crystals of $CaAl_2$ compound (a close partner of MgB_2 but with $MgCu_2$-type $C15$ structure) have been obtained[7] (*directly* from Ca_2Al_3 phase which has an eutectic point at $550°C$) and packed into a granular material (with single-phase granules ranging between 10 and $50\mu m$). Though no tangible superconducting signals were detected, a rather unusual transport properties have been found in these interesting compounds (see Ref.[7] for more details on sample preparation and actual measurements). In particular, the electrical resistance clearly exhibits a power-like (rather than exponential, expected for conventional low-temperature localization scenarios[8,9]) temperature behavior with resistivity $\rho \propto T^{-3/4}$ for $15K < T < 70K$ (Fig.3 in[7]), and decreasing almost linearly between 70 and $235K$ (Fig.2 in[7]). While the measured thermoelectric power (TEP) $Q(T)$ has a well-defined N-like form (Fig.4 in[7]) with $Q(T) \propto T^{1/2}$ below $60K$, $Q(T) \propto T^{3/4}$ above $100K$, and $Q(T)$ almost linearly *decreasing* with T in the intermediary regime (Fig.5 in[7]).

Turning to the interpretation of the above experimental results, we notice that the very fact that the resistance data do not follow conventional localization scenarios dominated by a variable-range-hopping (VRH) mechanism with resistivity $\rho(T) = \rho_0 \exp[(T_0/T)^p]$ (leading to either Mott-like[8] or Shklovskii-Efros-like[9] behavior with $p = 1/4$ and $1/2$, respectively) apparently hints at a relatively small value of the characteristic temperature T_0 in this material (so that $T_0/T \ll 1$ for the whole temperature interval $15K < T < 300K$). This, in turn, implies the importance of electron-phonon interaction effects on the hopping processes when localization is accompanied by formation of polarons (strongly polarized regions around electrons in the conduction band[10]). Recall that the binding energy of the polaron a distance R apart from a donor (or acceptor) site is given by $E = \alpha/4R = \hbar^2/2m_p a^2$ where $\alpha = e^2/4\pi\epsilon_0\epsilon$ with ϵ being the static dielectric permeability of the polarized crystal, m_p is an effective polaron mass, and $a = \hbar^2/m\alpha$ is the polaron size. At low temperatures (when the principal processes are dominated by the Debye energy $k_B\theta_D$), $E \simeq k_B\theta_D$ leading to scattering of phonons with "heavy" polarons (typically[8], $m_p \simeq 10m_e$ where m_e is a free carrier mass) implying a huge value of the dielectric permeability (for example, in doped titanates $\epsilon \simeq 1000$ leading to $a \simeq 30Å$). If we accept this argument, we will have to assume that in addition to the conventional thermally activated hopping between the neighboring unoccupied sites governed by correlated VRH-like processes with conductivity $\sigma_h(T,E) = \sigma_0(E/k_BT)e^{-U}$ (where $U = 2R/a + E/k_BT$ with R being the hopping distance, a localization length, and $E = \alpha/4R$ an energy difference between two localized states; $\sigma_0 = 4\nu e^2/\alpha$ with ν being a characteristic phonon frequency), we are dealing with the so-called phonon-assisted mechanism of metal-insulator transition (known to be active in slightly doped semiconductors with impurity conduction and other disordered systems[8,9]) which is a hopping process substantially modified by electron-phonon interaction controlled by the Debye temperature θ_D. (It is worth mentioning a somewhat similar mechanism in slightly doped manganites where spin polaron hopping is controlled by the exchange energy[11,12].) At high temperatures (for $T > \theta_D/2$), this contribution to the observed conductivity has a thermally activated form of $\sigma_{th-ph}(T,E) = \sqrt{\frac{\theta_D}{2T}}\sqrt{\frac{E}{2E_a}}\sigma_h(T,E)$ where $E_a \equiv E(R=a) = \alpha/4a$,

while at low temperatures (for $T < \theta_D/2$) the conductivity is governed by the phonon-assisted polaron hopping with $\sigma_{d-ph}(E) = \sigma_{th-ph}(T = \frac{1}{2}\theta_D, E)$. As we shall see below, the latter contribution dominates the temperature behavior of the resistivity and TEP data under discussion. Let us start with the resistivity. According to the above-mentioned scenario the observed temperature dependence of ρ should follow the law:

$$\rho(T) = \left[\sigma^{-1}(T, E)\right]_{E=E_0(T)} \tag{1}$$

where $\sigma(T, E) = \sigma_h(T, E) + \sigma_{th-ph}(T, E) + \sigma_{d-ph}(E)$, and $E_0(T)$ is defined via the temperature dependence of the minimal hopping distance $R_0(T)$. The latter is the solution of the extremum equation $dU(R)/dR = 0$ where $U(R) = \frac{2R}{a} + \frac{\alpha}{4k_BTR}$. Hence, $R_0(T) = (a/4)\sqrt{T_0/T}$, $E_0(T) \equiv E(R_0) = (k_BT_0/2)\sqrt{T/T_0}$, $U_0(T) \equiv U(R_0) = \sqrt{T_0/T}$, and $k_BT_0 = 2\alpha/a$. As a result, Eq.(1) can be written as follows

$$\rho(T) = \rho_0 \left(\frac{T}{T_0}\right)^{-3/4} \left[1 + \delta_1 \left(\frac{T}{T_0}\right)^{5/4} e^{\sqrt{T_0/T}} + \delta_2 \left(\frac{T}{T_0}\right)^{3/2} e^{\sqrt{T_0/T}}\right] \tag{2}$$

Here $\rho_0 = 8(\theta_D/T_0)e^{\gamma}\sigma_0^{-1}$, $\delta_1 = (T_0/4\theta_D)e^{-\gamma}$, and $\delta_2 = (2T_0/\theta_D)^{3/2}e^{-\gamma}$ with $\gamma = \sqrt{2T_0/\theta_D}$. As we shall see below, for $15K < T < 70K$ and the estimates of the model parameters (T_0, θ_D, and $\delta_{1,2}$), the second and third terms in the rhs of Eq.(2) can indeed be regarded as small corrections to the main $T^{-3/4}$ dependence found to dominate the observed resistivity.

Turning to the TEP data, we notice that like the previously discussed resistivity, the temperature dependence of the thermoelectric power $Q(T)$ will be controlled by the hopping energy $E_0(T)$ as well, so that

$$Q(T) = 3Q_c(T) + \frac{\pi^2 k_B^2 T}{3e}\left[\frac{d\ln\sigma(T, E)}{dE}\right]_{E=E_0(T)} \tag{3}$$

Here the first term accounts for concentration dependent contribution of the three processes with $Q_c(T) = Q_0 \ln(N_v/n)$ where $Q_0 = \pi^2 k_B/3e$, $N_v(T) = (2\pi m_p k_B T/\hbar^2)^{3/2}$, N is the number of sites, and $n \simeq \sqrt{NN_v}$ is the carriers (polarons) number density. Using the above-introduced definition of $\sigma(T, E)$, for the temperature range under discussion, from Eq.(3) we obtain

$$Q(T) = 3Q_c(T) + 2Q_0\left[\sqrt{\frac{T}{T_0}} + A\left(\frac{T}{T_0}\right)^{-3/4} + B\left(\frac{T}{T_0}\right)^{3/4}\right] \tag{4}$$

for the temperature behavior of the observed TEP. Here $A = \theta_D/4T_0$ and $B = \sqrt{T_0/\theta_D}$. It can be easily verified that, in agreement with the observations, the above expression for $Q(T)$ exhibits a maximum at $T_{max} = (3A/2)^{4/5}T_0$ and a minimum at $T_{min} = (A/B)^{2/3}T_0$. In view of the definition of the coefficients A and B and using the experimental value of the minimum temperature ($T_{min} = 100K$), we immediately obtain a reasonable estimate for the Debye temperature in this material, namely $\theta_D = 4^{2/3}T_{min} \simeq 250K$ (recall that for $CaAlSi$ $\theta_D \simeq 226K$[5,6]). Furthermore, using the observed values of the maximum temperature $T_{max} = 60K$ and the corresponding TEP extrema, $Q_{max} \equiv Q(T_{max}) = 23\mu V/K$ and $Q_{min} \equiv Q(T_{min}) = 17\mu V/K$, as well as an obvious relation between the concentration contributions, $Q_c(T_{min}) = Q_c(T_{max}) + (3/4)Q_0 \ln(T_{min}/T_{max})$, we obtain the following estimates of the model parameters: $T_0 = 10K$, $A = 6.25$, $B = 0.2$, $\gamma = 0.28$, $\delta_1 = 0.0075$, $\delta_2 = 0.015$, $c_{max} = N_v(T_{max})/N = 0.04$, and $c_{min} = N_v(T_{min})/N = 0.02$. It is worth mentioning that the latter estimates of concentrations (with $c \ll 1$) provide further evidence in favor of adopted here polaron concept[8] for explanation of the observed N-like TEP form. Returning to the resistivity, let us notice that the above estimates corroborate our conjecture about dominant character of the observed $\rho(T) \propto T^{-3/4}$ law for $15K < T < 70K$ temperature interval providing at the same time an estimate of the characteristic model conductivity $\sigma_0 = 16\pi\epsilon\epsilon_0\nu = 2 \times 10^6\Omega^{-1}cm^{-1}$ which gives $\nu = 4 \times 10^{14}s^{-1}$ for phonon frequency (using $\epsilon = 1000$). Besides, at high temperatures the model predicts a small increase of resistivity as $\rho(T) \simeq \rho_0\delta_1\sqrt{T/T_0}$, in agreement with the observations. Finally, the deduced estimate of the localization temperature $T_0 = 2\alpha a/k_B = 10K$ gives $a \simeq 40\AA$, $m_p = (\hbar/\alpha)^2(k_BT_0/2) \simeq 8m_e$ and $R_0 = a/4 \simeq 10\AA$ for the polaron size, polaron mass and hopping distance, respectively, and explains why the Shklovskii-Efros law $\rho(T) \propto \exp(\sqrt{T_0/T})$ is not seen in the resistivity data for the whole temperature interval $15K < T < 300K$.

In conclusion, a brief comment is in order on the role of grain-boundary effects in the transport anomalies under discussion. Polarized light microscopy analysis of this densely packed polycrystalline material revealed (Fig.1 in[7]) a dendritic structure with a well-defined crystalline phases within a single grain. Besides, the very fact that the adopted here polaron picture reasonably well describes *both* electric resistivity and thermoelectric power suggests a rather high quality of this material (which is also evident from its X-ray diagram shown in Fig.7 from Ref.[7]) with presumably narrow enough grain distribution and quasi-homogeneous low-energy barriers between the adjacent grains.

We gratefully acknowledge financial support from Brazilian agency FAPESP.

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, *Nature* **410**, 63 (2001).

[2] M. Imai, E. Abe, J. Ye, K. Nishida, T. Kimura, K. Honma, H. Abe, and H. Kitazawa, Phys. Rev. Lett. **87**, 077003 (2001).

[3] B. Lorenz, J. Lenzi, J. Cmaidalka, R.L. Meng, Y.Y. Sun, Y.Y. Xue, and C.W. Chu, Physica C **383**, 191 (2002).

[4] M. Imai, K. Nishida, T. Kimura, and H. Abe, Physica C **377**, 96 (2002).

[5] R.L. Meng, B. Lorenz, Y.S. Wang, J. Cmaidalka, Y.Y. Sun, Y.Y. Xue, J.K. Meen, and C.W. Chu, Physica C **382**, 113 (2002).

[6] B. Lorenz, J. Cmaidalka, R.L. Meng, and C.W. Chu, Phys. Rev. B **68**, 014512 (2003).

[7] M. Ausloos, M. Pękala, J. Latuch, J. Mucha, Ph. Vanderbemden, B. Vertruyen, and R. Cloots, J. Appl. Phys. **96**, 7338 (2004).

[8] N.F. Mott, *Metal-Insulator Transitions* (Taylor & Francis, London, 1990).

[9] B.I. Shklovskii and A.I. Efros, *Electronic Properties of Doped Semiconductors* (Springer, Berlin, 1984).

[10] J.M. Ziman, *Electrons and Phonons* (Oxford, Clarendon Press, 1962).

[11] S. Sergeenkov, H. Bougrine, M. Ausloos, and R. Cloots, JETP Lett. **69**, 858 (1999).

[12] S. Sergeenkov, M. Ausloos, H. Bougrine, and R. Cloots, JETP Lett. **70**, 481 (2000).